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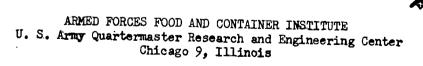
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A Study of Flavor of Irradiated Meat

Period: 14 January 1961 - 13 January 1963

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UNCLASSIFIED	 Radiation preservation of foods - Irradiation 	UNCLASSIFIED	UNCLASSIFIED .	UNCLASSIFIED
AD- Accession No.	BATTELLE MEMORIAL INSTITUTE Columbus 1, Ohio A STUDY OF THE FLAVOR OF IRRADIATED MEAT, by R. A. Kluter, V. G. Vely, and H. G. Schutz. Report No. 8 (Final) March 1963, 34 pp, 15 tables, 3 figures. (Contract DA-19- 129-QM-1734) AD Proj. 7-84-01-002. (Unclassified report)	Work accomplished during the entire contract period is reviewed in light of three major objectives: (1) evaluation and selection of methods for sample preparation and sensory panel presentation, (2) review, selection, and (over)	evaluation of psychophysical techniques for sensory panel studies, and (3) a review, selection, and study of chemical compounds identified in the volatiles of irradiated beef for their relative contribution to irradiation odor.	
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CONTRACT RESEARCH PROJECT REPORT

to

QUARTERMASTER FOOD & CONTAINER INSTITUTE FOR THE ARMED FORCES

QM Research and Engineering Command QM Research and Engineering Center, Natick, Massachusetts

Battelle Memorial Institute

Columbus, Ohio

Collaborators:

Robert A. Kluter Victor G. Vely

Howard G. Schutz

Project Number 7-84-01-002 Contract No. DA-19-129-QM-1734

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Title of Contract: A Study of the Flavor of Irradiated Meat

SUMMARY

Work accomplished during the 2-year contract period is reported in three major areas: (1) evaluation and selection of methods for sample preparation and sensory panel presentation, (2) review, selection, and evaluation of psychophysical techniques for sensory panel studies, and (3) review, selection, and study of chemical compounds identified in the volatiles of irradiated beef for their relative contribution to irradiation odor.

From various possible means of preparing and presenting chemicals for irradiation odor evaluation, the use of a fresh ground beef carrier, to which chemical(s) were added, was selected.

A sensory panel was selected and trained for the odor evaluations.

Of four psychophysical methods reviewed, two were used and evaluated during the project: (1) an intensity rating method, scaled from "none" to "extreme", to judge the quantity of irradiation odor contributed by chemicals, and (2) matching-standards technique, to determine qualitative odor attributes and to judge their degree of similarity to nine odor standards.

From literature reviewed, 29 chemical compounds were selected for study of their relative contribution to irradiation odor. Evidence from irradiation odor intensity data is presented which indicates that certain of the compounds studied may make a significant contribution to irradiation odor.

Suggestions are made for further work in the irradiation odor area.

FINAL REPORT

on

A STUDY OF THE FLAVOR OF IRRADIATED MEAT

by

Robert A. Kluter, Victor G. Vely, and Howard G. Schutz

INTRODUCTION

In the past decade, irradiation sterilization and/or pasteurization of foodstuffs has been investigated extensively by food technologists as either a replacement for or a supplement to thermal processing. Considerable credit for progress in this research area is due the Quartermaster Food & Container Institute, both for its internal research program and for coordination of a large outside contract program. However, one of the problems which has prevented the use of many irradiated meat products in military or civilian consumption is the presence of an undesirable flavor. This flavor has usually been implicated by a distinctive odor present in the meat product after the irradiation process.

Some progress in attenuating the effects of these flavors has been made by using odor scavengers, free-radical acceptors, chemical additives, sauces, and variations in the irradiation process; but the foregoing techniques have resulted in only a partial solution of the problem.

Volatile chemical substances, many of which are evidently produced during the irradiation process, have been isolated and identified. The list of compounds has included those produced during irradiation of both raw and precooked meats. These identifications prompted the Radiation Branch of the Quartermaster Food & Container Institute to embark upon an outside research program which would yield information about the relative contributions of these compounds to "irradiation flavor". It was thought that such information might provide a basis to control effectively the occurrence of irradiation flavor.

Battelle was awarded the present research program on January 14, 1961, and has since directed attention toward identifying the cause of the flavor problem in irradiated raw beef. Work has been concentrated primarily on evaluating the contribution to raw beef irradiation odor of selected single compounds and blends of compounds, using sensory panel techniques.

The research program has included (1) procurement, preparation, canning, and irradiation of raw ground tenderloin muscle (longissumus dorsi), (2) obtaining or synthesizing chemicals selected for study, (3) training of a sensory panel, (4) research on suitable psychophysical methods of evaluation, (5) development of a method for preparing and presenting experimental samples, (6) evaluation of the chemicals in the ground raw beef carrier both singly and in combinations, and (7) interpretation of results.

CHOICE OF BEEF CUT, CANNING, AND CONDITIONS OF IRRADIATION

Selection of Cut

Two criteria were found useful in selecting the most suitable cut of beef for this study: (1) the cut should be marbled uniformly throughout, which would be helpful whether used in the form of a roast or as a ground mixture and (2) for purposes of comparison, the cut should be one which was used as an experimental standard in previous beef research. The literature revealed that the longissumus dorsi or tenderloin muscle was commonly used to fulfill the above criteria.

During the odor studies, beef was purchased at approximately monthly intervals from Swift & Company, Columbus, Ohio. The grade purchased was usually U. S. Good; however, the quality of this grade was occasionally poor during 1962, making it necessary to buy the next higher grade, U. S. Choice (Swift's Premium). Procurement of matched pairs of tenderloins, one of each pair to be irradiated and one to be held as control beef, proved impracticable during the studies inasmuch as approximately twice the quantity of control beef was required to screen chemicals prior to panel evaluation and for actual panel studies. All beef was from steers and aged 24 to 48 hours, but the feedlot history of the animals could not be determined.

Preparation and Canning of Ground Beef

All beef was processed for canning on the day of procurement. The tenderloins were trimmed as much as practicable of all excess surface fat and connective tissue. The meat was then cut into large cubes and passed once through the 1/8-inch plate of hand-operated No. 10 Enterprise food chopper.

The ground raw product was immediately hand packed into washed 300 x 407 cans (14-ounce size), 12.5 ounces per can, a quantity which allowed at least a 1/2-inch head space under the lid for freezing expansion and gas formation during irradiation. The amount of product and head space allowance was calculated from a formula of a QMF&CI contractor, The American Can Company. The calculations indicated a can vacuum safety margin of 6 inches.

Before closing the cans, holes were punched throughout the ground beef to prevent the formation of air pockets inside the container. Lids were clinched on the cans with a bench model Dixie Automatic can sealer. This seam was not tight and allowed for air evacuation in the vaccum closing operation. The final stage of the closing operation was carried out in an Angelus 29V vacuum closing machine under a vacuum of 20 inches. This vacuum was the highest obtainable on the closing machine under conditions of continuous operation. A vacuum of 14 to 15 inches resulted in the sealed can.

Immediately after closing, the canned samples were quick-frozen in a -77 C Dry Ice-acetone bath for 1/2 hour. The freezing time was previously established as that time necessary to lower the center temperature of the container to at least -58 C. After

freezing, cans designated for irradiation were held in Dry Ice until time of shipment, and the control beef was transferred to a -26 C freezer.

Irradiation of Canned Ground Beef

To produce a standard irradiation odor impression, irradiation of the raw ground beef samples was carried out under controlled temperature conditions to minimize effects of odor development due to enzymatic or bacterial activity that might occur during the 46 to 53-hour period in the reactor. To accomplish the desired control, Dry Ice temperature conditions (-70 C) during irradiation were maintained. Shipment of samples to and from the irradiation site (Cook Electric Company) was made in cartons packed with Dry Ice. The dosage selected (5 x 10^6 rads) was sufficient to insure sterilization of the product and produce a readily recognizable irradiation odor.

Sample Containers

Previous work by the American Can Company under a QMF&CI contract revealed that either polybutadiene or epoxy phenolic can enamels containing zinc oxide paste performed well under ionizing radiations. Accordingly, a nearby canmaker (Heekin Can Company, Cincinnati, Ohio) was contracted to produce sufficient cans for the project with a polybutadiene enamel containing zinc oxide paste coated on 85-pound MCT-5 No. 25 electrolytic tin plate. The cans appeared to perform well under present experimental conditions.

SELECTION AND UTILIZATION OF CHEMICALS ASSOCIATED WITH IRRADIATION ODOR

Background

Relatively small amounts of chemical compounds formed by degradation under conditions of ionizing radiation contribute to irradiation odor of beef. Evidence accumulated through Quartermaster research programs indicated that proteins, peptides, and amino acids (according to the availability of the functional groups) were the major sources of the odors and flavors in irradiated meats. It was apparent, through attendance at a radiation contractor's meeting sponsored by the QMF&CI and the National Research Council, June, 1961, that general agreement existed as to the chemical causes of the odors.

The volatile compounds produced in beef by ionizing radiations fall into several classes: carbonyl compounds, sulfur compounds, hydrocarbons, nitrogen compounds, and alcohols. Carbonyls are believed to be derived from two sources in meat. The protein fraction produces carbonyls extractable with acidic salt solution, and the lipid fraction produces carbonyls soluble in organic solvents. A concurrent radiation-distillation technique has strongly implicated a reaction product of carbonyls with mercaptans or other sulfur-containing compounds as contributing to the off-flavor of beef. (1) Volatile

⁽¹⁾ Goldblith, S. A., and Wick, E. L., "Studies of Beef Irradiation Flavor Using a Concurrent Radiation - Distillation Technique", Report No. 8 (Annual), (1 May 1960 - 30 April 1961).

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sulfur compounds believed to be produced as a result of the destruction of methionine, cysteine, and cystine are also reported to be major contributors to the off-flavor and odor in irradiated beef. Hydrocarbons now appear to be significant in the odor complex of irradiated beef. In dilute concentration in air the hydrocarbons, hexane and hexene, were found to bear a resemblance to a "wet dog" type of odor. (2) Although volatile amines have been identified in irradiated beef, whether they contribute to flavor and odor changes has not been definitely established. Those volatile compounds produced in beef by ionizing radiation that have been identified quantitatively through mass spectrometry have been summarized(3) and are listed in Table 1. Other volatile compounds of beef have been reported in the literature with varying degrees of certainty and are given in Table 2.

Selection of Chemicals

Based on previous and continuing literature reviews, 29 chemicals representing the classes referred to previously were selected for study at Battelle. One chemical, β -methylthiopropionaldehyde (methional) was synthesized at Battelle according to the procedure of Patton and Barnes⁽⁴⁾. Two redistillations were made of the product, taking the fraction boiling at 64-65 C/ll mm. No significant fraction of lower boiling point was found. The dinitrophenylhydrazine derivative of this fraction melted at 123.5 C. Both the boiling point of the product and melting point of its derivative were somewhat higher than reported by Patton. Therefore, the product was checked by infrared analysis. The scan obtained was essentially identical to the infrared spectrum of methional given by Patton. The intense and lingering odor was typical of methional in the judgment of several technical people familiar with its odor. Therefore, this fraction was used in the Battelle study. The chemicals chosen for these studies are given in Table 3.

Selection of a Sample-Presentation Method

Evaluation was made of the physical parameters involved in the preparation of samples for panel evaluation. Several methods were examined to approximate the stimuli obtained through the presentation of the natural product, beef. Presentation of chemicals alone to a panel without a vehicle presented unnatural stimuli and in certain cases an odor of high intensity. During a preliminary subjective evaluation of the odor of several chemicals - propanal, n-propanol, nonanol, and guaiacol - it was apparent that either very small amounts (about 1 microliter) or significant dilutions of the chemicals were required to moderate the intensity of their odors. Diluents which were found effective under certain conditions were water, methanol, ethylene glycol, and mineral oil.

However, ethylene glycol was selected as the diluent for this study because it was odorless, and because all compounds selected for study, except octane, were soluble in it at the desired concentrations.

⁽²⁾ Merritt, C., Jr., et al., "Determination of Volatile Compounds Produced in Irradiated Meat", Pioneering Research Division, Quartermaster Research and Engineering Center, Report No. 5 (Annual), (1 July 1959 - 30 June 1960).

^{(3) &}quot;A Status Report of the Acceptability of Irradiated Beef", Radiation Project, Quartermaster Food & Container Institute (September 25, 1957).

⁽⁴⁾ Patton, S., and Barnes, I. J., "The Odor and Flavor of Methional", Food Research, 23, 221 (1958).

TABLE 1. VOLATILE COMPOUNDS OF BEEF IDENTIFIED BY MASS SPECTROMETRY

		Micromoles/Kilogram of Beef		
		Irradiated	Irradiated	
Compound	Unirradiated	2 Megarep	4 Megarep	
Acetaldehyde	(a)	23	170	
Pentanals		8.3	21	
Hexanals			6,5	
Heptanals			1,1	
Octanals			2	
Acrolein		8.8	23	
2-Methylacrolein		0.25	3.3	
Pentenals		Trace	Trace	
Hexenals	₩ ■	1.8	4.2	
Methylethyl ketone		9.7	22	
Hydrogen sulfide	4.3	23	39.6	
Methyl mercaptan	0.15	2.5	. 12	
Ethyl mercaptan	0.28	1.1	0.082	
Propyl mercaptan		1.5	0.59	
Butyl mercaptan		0.18	0.11	
Pentyl mercaptan			0.045	
Dimethyl sulfide			1.8	
Methylethyl sulfide			0.18	
Methylisopropyl sulfide		* **	0.15	
Diisopropyl sulfide			0.053	
Dimethyl disulfide		0.11	0.11	
Diethyl disulfide		0.0059	0.42	
Ethylisopropyl disulfide			0,10	
Diisopropyl disulfide		••	0.19	
Methanol	*	5	16	
Ethanol		14	39	
Ethylene		2:9	5.9	
Propylene	₩ ₩	2.9	4.4	
Pyrrole		0.22	0.32	
Pyridine		0.024	0.075	
Aniline		0.007	0.098	
Carbon dioxide	4500	1800	1500	
Carbon monoxide	110	33	65	
Benzene		0.74	4.9	
Toluene		0.13	0,34	
Ethyl benzene			0.048	
Isopropyl benzene			0.082	
Trimethyl benzene			0.082	
Butyl benzene			0.034	

⁽a) Not detectable.

TABLE 2. OTHER VOLATILE COMPOUNDS OF IRRADIATED BEEF REPORTED IN THE LITERATURE

Propanal	Octene
Glycidaldehyde	Octane
Nonanal	3-Methylthiopropional dehy de
2-Propanone	Carbon disulfide
2-Butenal	Carbonyl sulfide
Methylvinyl ketone	Isobutyl mercaptan
Propane	Methionine sulfoxide
Butene	Glutathione
Butane	Ammonia
Pentene	Methylamine
Pentane	Ethylamine
Hexene	N-Butylamine
Hexane	N-Amylamine
Heptene	Phenylethylamine
Heptane	Phosphotidyl ethanolamine

TABLE 3. LIST OF CHEMICALS SELECTED FOR A STUDY OF THE ODOR OF IRRADIATED MEAT

Carbonyl	Acetaldehyde Propanal Fentanal Octanal Nonanal 2-Propenal 2-Butenal 2-Propanone 3-Methylthiopropionaldehyde Hydrogen sulfide	Ditto Practical Grade Research Grade Ditto Eastman Grade Ditto Reagent Purified BP 64-65 C/11 mm	Distillation Products Industries Ditto " Aldrich Chemical Co. Ditto Distillation Products Industries Ditto J. T. Baker Chemical Company Ditto Synthesized at Battelle
Sulfur	Fentanal Octanal Nonanal 2-Propenal 2-Butenal 2-Propanone 2-Butanone 3-Methylthiopropion- aldehyde	Practical Grade Research Grade Ditto Eastman Grade Ditto Reagent	Aldrich Chemical Co. Ditto Distillation Products Industries Ditto J. T. Baker Chemical Company Ditto
Sulfur	Octanal Nonanal 2-Propenal 2-Butenal 2-Propanone 2-Butanone 3-Methylthiopropion- aldehyde	Research Grade Ditto Eastman Grade Ditto Reagent Purified	Aldrich Chemical Co. Ditto Distillation Products Industries Ditto J. T. Baker Chemical Company Ditto
Sulfur	Nonanal 2-Propenal 2-Butenal 2-Propanone 2-Butanone 3-Methylthiopropion- aldehyde	Ditto Eastman Grade Ditto Reagent Purified	Ditto Distillation Products Industries Ditto J. T. Baker Chemical Company Ditto
Sulfur	2-Propenal 2-Butenal 2-Propanone 2-Butanone 3-Methylthiopropion-aldehyde	Eastman Grade Ditto Reagent Purified	Distillation Products Industries Ditto J. T. Baker Chemical Company Ditto
Sulfur	2-Butenal 2-Propanone 2-Butanone 3-Methylthiopropion- aldehyde	Ditto Reagent Purified	Industries Ditto J. T. Baker Chemical Company Ditto
Sulfur	2-Propanone2-Butanone3-Methylthiopropionaldehyde	Reagent Purified	J. T. Baker Chemical Company Ditto
Sulfur	2-Butanone 3-Methylthiopropion- aldehyde	Purified	Company Ditto
Sulfur	3-Methylthiopropion- aldehyde	<u>-</u>	
Sulfur	aldehyde	BP 64-65 C/11 mm	Synthesized at Rattella
	Hydrogen sulfide		Symmestated at Dattelle
		Purified	The Matheson Company
	Carbon disulfide	Reagent	J. T. Baker Chemical Company
	Carbonyl sulfide	Purified	The Matheson Company
	Methyl sulfide	Eastman Grade	Distillation Products Industries
	Methyl disulfide	Ditto	Ditto
	Methyl mercaptan	II	11
	Propyl mercaptan	11	U
Hydrocarbon	Hexane	BP 68-69 C	Matheson, Coleman and Bell
	l-Hexene	99%, BP 63-64 C	Ditto
	Octane	99 + mol%	n
	1-Octene	Practical, BP 120- 122 C	11
	Benzene	Reagent	J. T. Baker Chemical Company
	Toluene	Reagent	Ditto
Nitrogen	Ammonia	Anhydrous	The Matheson Company
	Methylamine	40% in water	Distillation Products Industries
	Pyrrole	Research Grade	Aldrich Chemical Company
	Pyridine	Reagent	Mallinckrodt Chemical Works
Alcohol	Methanol	Absolute, Reagent	General Chemical Division, Allied Chemical
	Ethanol	200 Proof	Local Supplier

The most efficient and satisfactory sample-preparation technique utilized fresh ground beef to which the chemical(s), dissolved in ethylene glycol, were added. The following procedure was used to present chemicals for evaluation in all panel studies:

- (1) Fresh ground beef was thawed for approximately 2 hours under cool running water (the irradiated product was thawed under the same conditions).
- (2) One ounce of product was weighed into a brown-glass 250-ml jar (11.8 centimeters high, 4.8-centimeter-diameter mouth) and capped with an enameled metal lid, lined with a paraffin-coated board gasket. The lids and jars were commonly used in packaging foods such as soluble coffee. The lid gaskets were odorless, but to avoid the possibility of odor absorbtion, the lids were never used more than two times.
- (3) A 1-milliliter aliquot of a solution containing the desired microliter quantity of a chemical was delivered into the jar. For blending experiments each chemical was diluted separately and delivered in a separate 1-milliliter increment.
- (4) Mixing of meat with chemical additive(s) was accomplished with a fourblade Cenco Variable Speed Stirrer set at low speed.

Prior to panel presentation, preliminary work was conducted to determine a concentration of chemical(s) which would fulfill two criteria: (1) result in a detectable change from fresh beef aroma and yet (2) not result in an overwhelming odor characteristic of the chemical itself. It was found that some of the more voltile compounds, such as the aldehydes, increased in odor intensity as equilibrium was established in the head space of the jar. Concentrations were adjusted to allow for these occurrences.

All ground beef samples were kept as cool as possible during weighing and chemical addition operations. The samples were allowed to come to room temperature for I hour prior to panel evaluation and remained at that temperature no longer than 2 hours prior to evaluation. Each sample jar was opened once for evaluation and not reused by another panelist.

Panel Evaluation Methodology

Four psychophysical methods were considered in accomplishing two goals: (1) to characterize qualitatively and quantitatively irradiation odor emanating from raw ground beef irradiated at 5×10^6 rads and fresh ground beef, and (2) to determine the relative contribution single chemicals or chemical blends in fresh ground beef to the development of irradiation odor.

The methods, summarized from the First Quarterly Report, were as follows:

(1) A matching technique was proposed in which subjects would rate the similarity between an experimental sample and an irradiated beef standard on a "not similar" to "extremely similar" rating scale.

- (2) The rating scale determination of irradiation-like odor was considered. The most intense irradiation odor would be that of an undiluted irradiated beef sample and would be called "extreme". Experimental samples would then be judged against an irradiation odor intensity scale ranging from "none" to "extreme". The relative contribution of chemical(s) added to fresh ground beef would be judged by the mean irradiation odor intensity rating. Use of this method should produce a single qualitative judgment concerning the irradiated and experimental samples without regard to specific attributes of irradiation odor.
- (3) A third psychophysical method proposed would supply individual attribute judgments. Panelists would freely associate irradiated beef odor with various adjectives which would be screened for frequency and appropriateness to the task. Each attribute would then be associated with an intensity scale, ranging from "none" to "extreme". Panelists would rate irradiated beef odor against these rating scales, yielding a set of dimensions for irradiation odor. Experimental samples would be rated in the same way. The observed similarity of odor dimensions of an experimental sample to the dimensions of the irradiated beef standard would be a measure of the experimental sample's importance to irradiation odor.
- (4) A fourth method would use information on odor factors obtained under Contract DA-19-129-QM-1500 and was called the matching-standards technique. Nine odor standards representing the same number of odor attributes would be selected. The method would be used to characterize an irradiated beef sample by rating the degree of similarity of its odor to each of the nine standards. Experimental samples would be rated against the same set of standards. Similarity of odor dimensions between irradiated and experimental beef samples would be a measure of the contribution of the selected chemical(s) to irradiation odor.

Methods (2) and (4) were selected to yield both qualitative and odor-dimension information about irradiated beef odor. Their relative usefulness and value in this study will be subsequently discussed.

In the First Quarterly Report, Method (1) was discarded because it would have required an irradiated beef sample for every evaluation session, involving extensive time and costs. However, an equal amount of irradiated beef was required when Method (2) was used. Thus, the reason for discarding Method (2) was not valid. The use of Method (1) should be considered in future studies if an over-all qualitative judgment is desired.

A persistent problem with the free-association method in work on other food products has been the variable meanings among panelists of the adjectives used for the intensity scales. Such variability does not ordinarily present a great problem when a large group of subjects participate, but it can hamper the discrimination of odor differences. Thus, it was felt that Method (3) would not be useful in the present study.

Selection and Training of the Irradiated Beef Panel

Fifty people from the Battelle staff who volunteered for the meat panel were screened for their abilities in (1) rating odor intensities, and (2) matching similarities of unknown odors to a group of nine standard odors.

The compound used in the first test was 1-propanol, one of the nine standards used in the odor-matching study previously reported. This material had the advantage of being completely soluble in water for the range of dilutions desired.

Four dilutions of propanol were made up, representing a geometric series of dilutions from full strength which differed by a factor of 1/3. Thus, the dilutions were 1/3, 1/9, 1/27, and 1/81. The solutions had the advantages of (1) requiring sensitivity to pick up an odor (1/81 dilution), (2) requiring good sensitivity to discriminate at low concentrations (1/27 and 1/81), and (3) giving a fair chance to discriminate at high concentrations (1/3 and 1/9).

Before presentation of the dilutions to the panelists, an undiluted sample was first presented and the panelists told that this odor intensity represented the "extreme" value and that no odor to be rated would be more intense than this. The rating form used was a simple nine-point intensity rating scale ranging from "none" to "extreme". All panelists were presented the dilutions in ascending odor of dilution. Dissimilar codes were given panelists in any one session to avoid problems of communication inside and outside the panel facilities about the nature of the test.

Of the 50 people who appeared for the first test, 35 were selected for further testing on the basis of three criteria: (1) those who rated the four dilutions correctly in ascending order (N=18); (2) those who rated the 1/27) and 1/81 dilutions equally or one scale mark either way, the other dilutions being correctly rated in order (N=4); and (3) those who rated the first three dilutions in correct order but rated the 1/3 dilution equal to or less than the third (N=13).

For the second sensory test in the panel screening sessions, the matching-standards technique described in the report of 11 August 1961 was used. Use of this method resulted in not only a test situation but also a training session in the use of the method itself. Three consecutive sessions were run, one per day, with one unknown presented each day. The unknowns were the same on the first and third days to check for reliability in the similarity ratings; the unknown on the second day was used mainly to prevent familiarity with the same two unknowns and as additional training.

Nonanol was selected as the unknown to repeat because it seemed very similar to one of the standards, heptanol (oily), as well as bearing slight similarities to 1-propanol (etherish) and hexanol (metallic). This resulted in a fairly straightforward rating problem. The other compound, propionaldehyde, seemed to have subtle qualities bearing slight resemblance to a number of standards, thereby also resulting in a challenging test situation. Instead of arranging the standard odors in ten randomizations, as will be described in a validation study of the odor-matching technique, they were arranged for this and all succeeding odor-matching studies in the order of adaptation rate (from least to highest rate, see Table 4). The rating form, used for this and all subsequent evaluations, is shown in Figure 1.

FIGURE 1. ODOR-DIMENSION ANALYSIS

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TABLE 4. ARRANGEMENT OF ODOR DIMENSION ANALYSIS STANDARDS ACCORDING TO ADAPTATION RATE (UNITS OF ODOR INTENSITY/MINUTE)

Odor Quality	Chemical	Concentration, per cent(a)	Adaptation Rate
Oily	Heptanol	100	0.174
Sweet	Vanillin	100	0.180
Fragrant	Methyl salicylate	100	0.198
Spicy	Benzaldehyde	100	0.264
Burnt	Guaiacol	100	0.300
Rancid	Butyric acid	3,8	0.360
Metallic	Hexanol	100	0.384
Etherish	I-Propanol	100	0.432
Sulfurous	Ethyl disulfide	0.03	0.438

⁽a) Dilution made by volume.

Criteria for final selection of the panel consisted of calculating a simple absolute "D" score (to be described in the following section of this report) of each individual between the two rating performances with nonanol. In addition, an average was calculated for each similarity attribute. The 26 people were selected according to the smallest differences between performances individually and the smallest differences from the average test-group performance for each attribute.

VALIDATION STUDIES OF PSYCHOPHYSICAL METHODOLOGY

Methods (2) and (4), mentioned previously, were evaluated for their reliability and validity in determining the qualitative and odor-dimension characteristics of irradiated beef.

Irradiation Odor Intensity

The usefullness of an irradiation odor intensity rating scale was tested by "diluting" raw irradiated ground beef with portions of fresh ground control beef. Dilutions selected and tested as unknowns were 50-50 and 25-75 irradiated control beef combinations and a fresh ground beef sample.

Ground beef samples were blended, and 1-ounce portions weighed into the sample jars previously described. Evaluation was carried out by the trained panel according to the following steps:

(1) They were given a jar marked "Std" which was the undiluted irradiated beef sample. They were asked to sniff the contents of the jar and consider the odor from it to be the "Extreme" (scored 8) in irradiation odor intensity. This sample was not rated.

- (2) After establishing the irradiation odor intensity of the standard, the panelists then received, one at a time, three unknowns to be rated, in a serial order balance. The rating form used for these studies is shown in Figure 2.
- (3) In this irradiation odor intensity study, panelists were not allowed to refer to the standard between evaluations of unknown samples. However, it later became evident that they lacked confidence in ratings for the second and third presentations, and that the first sample was given the advantage of being evaluated immediately after the encounter with the standard (although each unknown sample was given this advantage an equal number of times). Panelists were thus allowed to refamiliarize themselves with the odor of the standard prior to evaluation of each unknown. In this instance, the problem of memory was probably more serious than the problem of adaptation.

A 30-second rest was given between presentations to minimize adaptation effects. Panelists were instructed that the irradiation odor intensity of the samples would not exceed the "Extreme" value of the standard. This procedure was utilized to evaluate the effects on irradiation odor intensity of chemicals added to fresh ground beef throughout this program.

Results of the irradiation odor dilution study are presented graphically in Figure 3. It was evident that the panel could discriminate different intensities of irradiation odor under the experimental conditions described. It appeared initially that the irradiation odor intensity value for the control ground beef was much too great. However, the presence of a "background" odor in irradiated beef was not discounted during the course of this project, either by literature review or contacts with Quartermaster personnel. In addition, the value observed in Figure 3 did not vary significantly from values obtained from periodic re-evaluations of control beef. These observations may be further evidence that the characteristic "beefy" odor of fresh ground beef contributes to the over-all irradiation odor impression.

Evaluation of Matching-Standards Technique

Purpose

The purpose of this experiment was to determine the reliability and validity of a matching-standard technique for characterizing odorant dimensions.

Materials

Six ten-hole wooden racks were prepared, each containing nine 8-dram vials (15-mm mouth) into which was placed 5 milliliters of each standard solution. The tenth hole was used to hold the unknown solution. Table 5 gives the compound, purity, and source of the standards and the unknowns. The standards were chosen on the basis of studies conducted at the QMF&CI and Battelle and represented nine basic odor types.

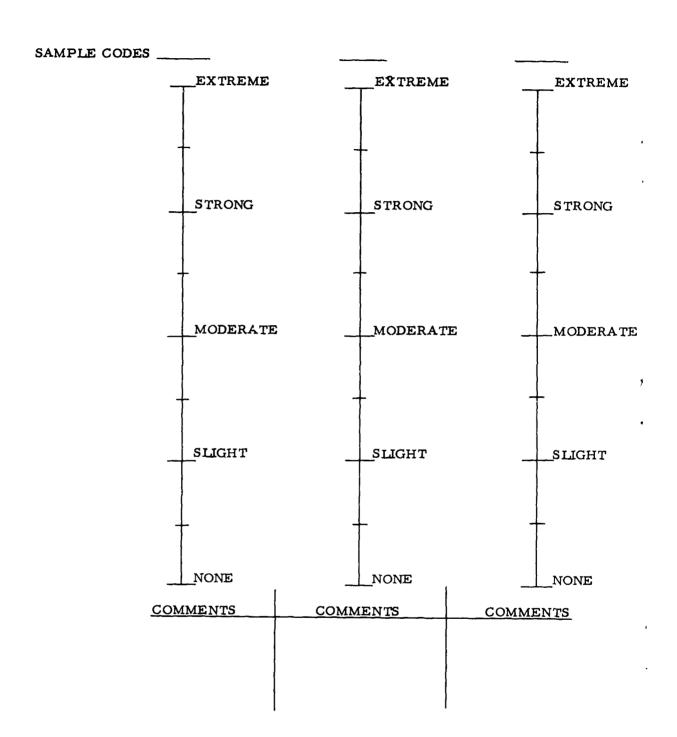


FIGURE 2. IRRADIATION ODOR INTENSITY

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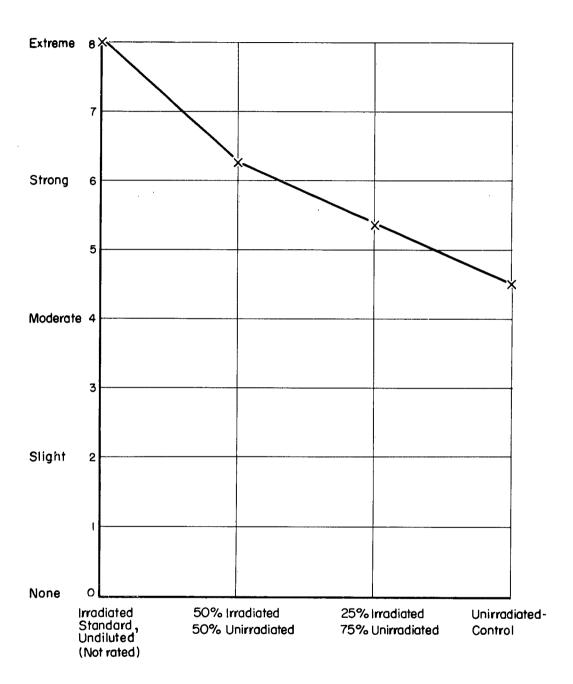


FIGURE 3. IRRADIATION ODOR INTENSITY

Each "X" is the mean of 23 judgments.

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TABLE 5. LIST OF CHEMICALS USED FOR THE ODOR-DIMENSION ANALYSIS

Chemical	Purity	Supplier
	Standards	
Methyl salicylate	99.7%	Matheson, Coleman and Bell
i-Propanol	Reagent	J. T. Baker Chemical Company
Vanillin	99.9%	Matheson, Coleman and Bell
Gauiacol	Highest feasible	Matheson, Coleman and Bell
Butyric acid (3.8 per cent)(a)	Eastman Grade	Distillation Products Industries
Heptanol	Highest feasible	Mathesom, Coleman and Bell
Hexanol	Purified	J. T. Baker Chemical Company
Benzaldehyde	98.6 per cent chlorine-free	Matheson, Coleman and Bell
Ethyl sulfide (0.03 per cent)	98.1%	Matheson, Coleman and Bell
	Unknowns	
Isosafrole	98.5%	Matheson, Coleman and Bell
Benzyl acetate	99.3%	Matheson, Coleman and Bell
L-Menthol	Meets U.S.P. specifications	Matheson, Coleman and Bell
I-Octanol	Highest feasible	Matheson, Coleman and Bell
Butylamine (1.8 per cent)	Highest feasible	Matheson, Coleman and Bell
Alpha picoline (2.4 per cent)	Pure	Union Carbide Chemicals Company
Pyridine (9.8 per cent)	Reagent	Mallinckrodt Chemical Works
Amyl acetate	Purified	J. T. Baker Chemical Company
Methyl ethyl ketone	Purified	J. T. Baker Chemical Company
Paradichlorobenzene	Mp, 52 to 54°C	Matheson, Coleman and Bell

⁽a) Designates concentration of chemical, per cent by volume. Water used as diluent.

Ten substances were chosen as unknowns to be characterized by use of a matching technique. They were selected on the basis of three criteria:

- (1) They represented different chemical structures.
- (2) Both pleasant and unpleasant odorants were represented.
- (3) Some were quite similar in smell, others disimilar. This was estimated by use of an intercorrelation matrix computed from ratings of 29 odorant attributes on a group of 30 odorants at the QMF&CI. The matrix of correlations for these ten materials is shown in Table 6.

TABLE 6. INTERCORRELATION MATRIX FOR TEN UNKNOWNS, RHO'S

	Butrylamine	α-Picoline	Isosafrole	Benzyl Acetate	Amyl Acetate	Pyridine	Methyl Ethyl Ketone	Paradichlorobenzene	1-Octanol	\$-Menthol
Butylamine		0.83	-0.61	-0.65	-0.50	-0.62	-0.06	-0.07	0.20	-0.49
α-Picoline			-0.72	-0.72	-0.45	0.80	-0.08	0.02	0.21	-0.58
Isosafrole				0.78	0.50	-	-0.29	-0.13	-0.23	0.60
Benzyl Acetate					0.76	-0.63	-0.22	-0.30	-0.20	0.42
Amyl Acetate						-0.31	0.07	-0.30	-0.06	0.33
Pyridine							0.12	-0.09	0.16	-0.53
Methyl Ethyl Ketone								0.35	-0.17	0.30
Paradichlorobenzene	;								-0.38	0.35
l-Octanol										-0.49
L-Menthol										

The rating form and attribute names shown previously were utilized with certain modification. For this experiment, ten random orders of the nine-attribute scales were devised and made up as separate forms. The use of these random lists is explained in "Testing Procedure".

Subjects

The twenty subjects (not the same panel used for the irradiation odor study) included 6 women and 14 men, all of whom had previous experience in making various psychophysical judgments. However, none was familiar with the techniques employed in the present study. Some were chemists while others had no professional connection with odorous materials. They could be said to represent a semisophisticated group whose experienced and training level was probably closer to a naive consumer population

than to the level required to use the matching-standards technique. They had, however, been previously screened for ability to discriminate other food odors and flavors and had experience with qualitative free-association techniques.

Experimental Design

A presentation order was devised in which each of the 20 subjects would receive the ten unknowns twice. The 20 presentations were randomized for each subject and divided into five sessions; four samples were presented per session. Two restrictions were placed on the randomizations: (1) an odorant could not be given twice per session to the same subject, and (2) each of the ten unknowns appeared an equal number of times in each of the four testing positions for both the first and second presentations. These two restrictions assured that errors due to order of testing would be minimized.

To control the occurrence of fatigue, adaptation, or motivation factors which might have affected the reliability or sensitivity of the method, ten orders of attributes were assigned to each of the ten unknown odorants. Thus, each unknown would be evaluated twice under each attribute order for each of the two times presented.

Testing Procedure

The five sessions were conducted over 5 consecutive days, each subject testing once a day. Sessions were held both morning and afternoon between 9:30 and 11:00 a.m. and 2:00 and 4:00 p.m. in an air-conditioned room. Subjects sat in individual booths that gave visual separation from each other. They were informed that they were testing a method of classifying odors, and that they would receive 20 substances to classify. The duplication of each unknown was not mentioned. The procedure for a subject during a session was as follows:

- (1) The subject received the rack of odor standards and smelled each one, associating the appropriate name given on a rating form.
- (2) He received the first unknown and another rating form with one of the ten randomizations for the odor standards. He arranged the standards in the rack according to their position on the rating form he had received.
- (3) He then sniffed the unknown, being careful not to touch his nose to the vial.
- (4) He sniffed the first standard, using the same precaution as in Step (3), and rated the degree of similarity of the unknown to that standard.
- (5) Waiting approximately 30 seconds, he sniffed the second standard and rated, then the third standard and rated.
- (6) After the third standard, the subject sniffed the unknown again and then went through the fourth and fifth and sixth standards. After the sixth rating he sniffed the unknown again and went through the last three standards.

(7) The subject was given 45 seconds between unknowns, then repeated Steps (2) through (6).

Each of the five sessions was conducted in the same manner, the subject refamiliarizing himself with the standards first. About 20 minutes were required for the subject to finish the four unknowns per session.

Experimental Controls

Sample Controls:

- (1) Six vials of each unknown were available for each session. Care was taken to not use an unknown more than once an hour to allow sufficient time for re-establishment of an equilibrium in the headspace of the vial.
- (2) Each set of six unknowns was given a different number so that the code might not be utilized as a clue to the repetition of samples.

Environmental Controls:

- (1) The room temperature was maintained at 72 ± 5 F.
- (2) A charcoal air filter with a power-driven fan was in operation throughout the test period.
- (3) No smoking was allowed in the test room.

Subject Controls:

- (1) Subjects were required to wash their hands before each test session.
- (2) Subjects were asked not to use strongly scented perfumes and lotions during the week of testing.

Results and Discussion

Analysis of the Data. The ratings for each unknown were converted to numerical values, 0 to 8, and averaged over the 20 subjects for the first and second presentation. The following statistics were computed:

- (1) The rank order correlations (rho) for each unknown between the degree of similarity means of the first and second presentations for the nine standard comparisons.
- (2) The index of similarity "D" among all unknowns; D is the square root of the sum of the squared algebraic difference between the dimension means of two unknowns.

TABLE 7. MEANS ON 10 CHEMICALS OVER 20 SUBJECTS

								 		Unknow
	Isosa	frole	Benzy	Acetate	ℓ-ме	nthol	Oct	anol	Butylamine	
Characteristic	1	2	1	2	1	2	1	2	1	2
Fragrance	3.30	3.05	2.00	2, 10	3.40	3.85	1.65	1.05	0.50	0.90
Etherish	0.90	1.05	1.45	2, 15	1.30	0.95	0.85	0.95	2.40	1.90
Sweet	2.65	2.75	1.95	1,95	1.65	1.95	0.85	0.90	0.40	0,65
Burnt	1, 15	1.25	1.05	0.30	0.95	0.55	0.60	0.95	0.90	0.75
Rancid	0.05	0.35	0,55	0.25	0.15	0.15	0.25	0.40	1.40	1,50
Oily	2.05	1.85	2.60	3,10	1.75	1.50	5.80	6.45	2.05	1.65
Metallic	1.65	1.95	2.55	2.75	1.80	1.85	3.50	3.20	2,05	1.90
Spicy	2.75	2.75	2.55	2.20	2.75	3.15	1.40	1.05	0.70	0.90
Sulfurous	0.25	0.15	0.25	0.70	0.25	0,15	0.60	0.65	1.75	1.05
Rho	.0.	96	0.9	90	0.9	95	0.9	94	0.	92

ON EACH OF TWO PRESENTATIONS

Alpha P	icaline	Pyridine Amyl Acetate				Methyl Keto	-	Paradichloro- benzene		
1	2	1	2	1			2	1	2	
0.35	0.25	0.30	0.30	2.05	2.15	1,40	1.20	1.55	1.90	
1,40	1.00	1.85	1.30	2.70	2,70	4, 10	5.00	1.50	1.45	
0.40	0 .4 0	0.40	0.40	1,50	1.70	0.95	0.60	1,25	1.30	
1.25	0.85	0,95	0,90	0.55	0.65	0.80	0.80	1,00	0.70	
0.95	1,20	1.95	1,95	0.40	0.25	0,35	0.20	0.30	0, 20	
1.90	1,85	1.50	1.65	1.85	2,80	1.85	2.15	1.40	1, 18	
2.45	2.35	2.85	1.60	1.95	3,10	3,40	3.25	1.25	1.40	
0.75	0.80	0.70	0.45	2.15	2.10	1,55	1.20	1.55	1.68	
3.90	2.45	3.20	4.00	0.40	0.30	0.50	0.65	1.05	0.35	
0.9	5	0.99	2	0.7	3	0.9	5	0.9	2	

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15.2*

(3) The rho between the intercorrelations in Table 2 and the D values obtained in Step (2).

The first set of rho's gives a measure of group reliability of the test-retest type while the second set of rho's gives a crude measure of validity using the intercorrelation matrix as a criterion.

Reliability. The means for the ten unknowns on each of two presentations for each dimension are shown in Table 7. Examination of this table revealed a high degree of consistency between first and second presentation means. The rank order correlation coefficients (rho's) are given at the bottom of the column for each unknown. These ranged from 0.73 to 0.96; the median rho over all chemicals was computed as 0.93. All the rho's but one were significantly different from 0 at the 1.0 per cent level of confidence. The high reliability demonstrated was taken as evidence of the value of this technique for irradiation odor measurement.

Validity. The D values for each combination of the ten unknowns are given in Table 8. The D's were computed using the mean for the two presentations since high reliability was demonstrated. An example of the concurrent validity or discrimination power of the technique can be seen by noting the differences in dimension scores in Table 7 between odorants which have highly similar odors such as butylamine and pyridine. The face validity of the dimension scores is evident from the relatively low D scores between odors which are usually thought to be similar in smell and the relatively high D scores for odorants usually thought to be dissimilar in smell (Table 8).

The construct validity was obtained by the same method mentioned previously, this time by computing the rho's between the intercorrelations obtained in the QMF&CI study and the present D scores for each unknown. These rho's are shown in Table 9. The fact that some chemicals had low validity coefficients might be partly attributable to differences in purity of chemicals used in the two studies.

Table 10 gives the results of an odor dimension analysis of irradiated, control, and two irradiated-control dilutions. Samples were prepared in the same way as for the reliability test on the irradiation odor intensity method.

The statistic D was calculated as an index of the degree of difference between irradiated versus control, 50-50, and 25-75 dilutions. As could be expected, the smallest D occurred between irradiated and the 50-50 dilution, and the largest between the irradiated and control beef.

It was noted that the odor of irradiated beef was not highly similar to any of the nine odor standards. However, it appeared that the oily, sweet, and burnt attributes might be of some importance. It was assumed that if chemical additions to fresh ground beef resulted in higher similarity ratings for the attributes, the interpretation could be that the odor impression produced was not similar to irradiation odor.

TABLE 8. D MATRIX FOR 10 UNKNOWNS

	Butylamine	a -Picoline	Isosafrole	Benzyl Acetate	Amyl Acetate	Pyridine	Methyl Ethyl Ketone	Paradichlorobenzene	1-Octanol	l -Menthol
Butylamine		2, 15	4.38	3,14	2,84	1,19	3, 23	2,33	4.93	4,37
a-Picoline			$5_{\bullet} 25$	4, 15	3, 96	$1_{\bullet}12$	4, 55	3,46	5, 26	5, 29
Isosafrole				2.14	2.60	$5_{\bullet}82$	4.95	$2_{\bullet}60$	5, 41	1, 17
Benzyl Acetate					1, 15	$4_{\bullet}77$	3, 09	2,36	3, 88	2.37
Amyl Acetate	* .					$4_{\bullet}72$	2.47	2.17	4, 18	2.57
Pyridine		•					4, 83	4,01	5, 97	5, 98
Methyl Ethyl Ketone								3,80	5, 52	4,82
Paradichlorobenzene									5, 21	2,54
1-Octanol										5,64
← Menthol										

TABLE 9. VALIDITY COEFFICIENTS FOR 10 UNKNOWNS USING QMF&CI DATA AS CRITERION

Substance	Rho
Isosafrole	0.83
Benzyl acetate	0.82
ℓ -Menthol	0,92
1-Octanol	0.40
Butylamine	0.40
α -Picoline	0.56
Pyridine	0.55
Amyl acetate	0.58
Methyl ethyl ketone	0.20
Paradichlorobenzene	0.00

TABLE 10. ODOR-DIMENSION ANALYSIS OF IRRADIATED, CONTROL, AND TWO DILUTIONS OF IRRADIATED GROUND BEEF

Standard	Deg	ree of Similarity f	or Indicated Samp	le
Odor	Irradiated	50-50	25-75	Control
Oily	2.19	2.05	2.05	1.62
Śweet	1.10	0.71	0.67	1.10
Fragrant	0.24	0.19	0.19	0.33
Spicy	0.33	0.38	0.10	0.57
Burnt	0.90	0.71	0.33	0.33
Rancid	0.81	0.67	0.67	0.76
Metallic	0.86	0.62	0.67	0.86
Etherish	0.57	0.43	0.43	0.14
Sulfurous	0.43	0.43	0.05	0.14

Index of Difference (D)

$$D = \sqrt{\Sigma d^2}$$

Irradiated vs. 50-50 = 0.56 Irradiated vs. 25-75 = 0.90 Irradiated vs. Control = 0.99

EVALUATION OF SINGLE-CHEMICAL ADDITIONS TO GROUND BEEF

Irradiation Odor Intensity Studies

Irradiation odor intensity was determined for the 29 selected chemical compounds. Various concentrations of each substance were screened in the fresh ground beef carrier prior to panel presentation. Selection of an appropriate concentration was guided by criteria previously described and concentration data from Table 1.

Results of the irradiation odor intensity studies are presented in Table 11 in order of decreasing intensities. To simplify the blending experiments, the first 11 compounds were selected for intensive study. The 4.0 level for irradiation odor intensity appeared to be a logical cut-off value, because the periodic checks on fresh ground beef confirmed the existence of a "background" odor which was considered irradiation-like by panelists. Thus, it was assumed that substances which raised the irradiation odor intensity level above 4.0 contributed an irradiation-like quality to the odor above that contributed by fresh ground beef alone. The substances which rated below the 4.0 level were not of immediate interest in the blending experiments.

Comparison of the first 11 compounds listed in Table 11 with the compounds identified by mass spectrometry in Table 2 indicated that the following substances may be partly responsible for irradiation odor of beef irradiated at 5×10^6 rads (dosage for the current project): acetaldehyde, acrolein, hydrogen sulfide, 1-propanethiol, (propyl mercaptan), methyl sulfide (dimethyl sulfide), and pyridine. Thus, these sensory data may be further evidence for the presence in irradiated beef of some substances identified by instrumentation.

Odor-Matching Studies

The 29 selected chemicals were submitted individually in fresh ground beef to a panel evaluation of odor dimensions. One modification, the dilution of the nine standard odors (Table 12), was introduced for the following reasons:

- (1) Most of the odorous compounds seemed too intense to enable panelists to detect subtle amounts of a similar odor quality in an unknown beef sample. Panelists had also complained about the odor intensities.
- (2) Dilution of the standards to a level which retained the same odor quality appeared advantageous because of the possibility of adaptation. Previously, all standard odorants had been used at full strength except butyric acid and ethyl disulfide which had been diluted to 3.8 and 0.03 per cent, respectively.
- (3) Familiarity with the standard odors based on physical qualities such as solution color (quaiacol, with age) and crystalline form (vanillin) was reduced, since the two compounds mentioned were colorless and soluble in the ethylene glycol diluent.

TABLE 11. CONCENTRATIONS IN FRESH GROUND BEEF AND IRRADIATION ODOR INTENSITY MEANS ARRANGED FROM HIGH TO LOW INTENSITY FOR 29 CHEMICALS

Position	Compound	Concentration(a)	Irradiation Odor Intensity Mean(b
(1)	Pyridine	0, 2	5, 00
(2)	Hydrogen sulfide(c)	5.0	4.94
(3)	Propanal	0.05	4.72
(4)	Methylamine	0.50	4.58
(5)	Acrolein	0,3	4,42
(6)	Methional	0.2	4.32
(7)	2-Butenal	1.0	4.32
(8)	1-Propanethiol (propyl mercaptan)	0.002	4.25
(9)	Carbon disulfide	0.5	4.24
(10)	Methyl sulfide (dimethyl sulfide)	0.05	4, 16
(11)	Acetaldehyde	0,3	4.05
(12)	Methanethiol	0.002	3.89
(13)	2-Propanone	30.0	3.71
(14)	1-Octene	1.0	3.71
(15)	Octane	5.0	3.68
(16)	Ammonia (d)	50.0	3.65
(17)	Pyrrole	10.0	3.63
(18)	Nonanol	0.1	3.63
(19)	Methyl disulfide	0.075	3,63
(20)	Hexane	100.0	3.53
(21)	Carbonyl sulfide (e)	50.0	3.50
(22)	2-Butanone	2.0	3.43
(23)	n-Valeraldehyde	0.2	3.25
(24)·	Methanol .	500.0	3.21
(25)	Octanal	0.05	3.19
(26)	Benzene	5.0	3.05
(27)	Ethanol	500.0	2.94
(28)	l-Hexene	1.0	2.48
(2 9)	Toluene	3.0	2.47

⁽a) Concentration in $\mu 1$ of undiluted, pure chemical added per ounce of raw ground beef.

⁽b) Mean values obtained from ratings of 16 to 22 panelists. Word categories were scored from None = 0 to Extreme = 8.

⁽c) Hydrogen sulfide gas was bubbled through ethylene glycol. Per cent hydrogen sulfide obtained was 1.64.

⁽d) Ammonia gas was passed into water. Per cent ammonia obtained was 3,21. A 1:10 dilution was made for addition to ground beef.

⁽e) Carbonyl sulfide gas was bubbled through ethylene glycol. Per cent carbonyl sulfide obtained was 1.18.

TABLE 12. LIST OF CHEMICALS AND THEIR CONCENTRATIONS USED AS STANDARDS FOR THE ODOR-DIMENSION ANALYSIS^(a)

Tube	Attribute	Chemical	Concentration, per cent
1 .	Oily	Heptanol	1.0
2 .	Sweet	Vanillin	10.0
3	Fragrant	Methyl salicylate	1.0
4	Spicy	Benzaldehyde	5.0
5	Burnt	Guaiacol	0.5
6	Rancid	Butyric acid	0.1
7	Metallic	Hexanol	0.5
8	Etherish	1-Propanol	20.0
9	Sulfurous	Ethyl sulfide	0.005

⁽a) Purity of the chemicals was the highest available. Ethylene glycol, A.R. grade, was used as the diluent in all cases.

Comparison of odor-dimension results using undiluted and diluted odor standards indicated that mean similarity ratings were not affected. For example, the D score (index of similarity) between two irradiated beef samples, both matched with undiluted odor standards, was 0.61; between two irradiated beef samples, one analyzed against undiluted (one of beef samples from previous example) and one against diluted odor standards, the D score was 0.68.

Odor dimensions of the 29 compounds are presented in Table 13. For comparison of irradiation odor intensity levels with the D values, the chemicals are listed in the same order as in Table 11. It was evident, both from examination of Tables 11 and 13 and the calculation of a correlation coefficient, that no predictable relationships existed between the mean irradiation odor intensity values and the D values.

EVALUATION OF CHEMICAL BLENDS IN FRESH GROUND BEEF

Based on the irradiation odor intensity results from single-chemical presentations in fresh ground beef, the 11 compounds mentioned previously, which scored above 4.0 in irradiation odor intensity, were selected for blending into combinations of two or more. Initially, the 55 (combination of 11 items taken two at a time) possible two-member blends were screened in the laboratory and those determined to be of interest were evaluated by the trained sensory panel. To increase the number of blends which could be evaluated by the panel, the matching-standards technique was not used in this work. It was felt that the rating of irradiation odor intensity gave a more realistic appraisal of whether odors contributed by chemicals were irradiation-like. It was proposed that the matching standards be used when a relatively high (5.0 and above) irradiation odor intensity level had been reached, but time did not permit its further use.

Samples for panel presentation were made up as previously described, each chemical being added to the ground beef in the appropriate microliter amounts in 1 milliliter of solution. Results of the two-chemical blending experiments are presented in Table 14.

Thirteen of the two-chemical blends rating 4.0 and above for irradiation odor intensity were selected for multiple blending experiments in which three or more chemicals were combined in the ground beef. The data in Table 15 concluded the experimental work under this contract.

GENERAL DISCUSSION

The following discussion will evaluate the results of this study in light of three major objectives: (1) method of sample preparation and presentation, (2) sensory evaluation methodology, and (3) the contribution to irradiation odors of selected chemicals compounds isolated from irradiated beef.

TABLE 13. ODOR DIMENSIONS OF SINGLE CHEMICAL ADDITIONS TO RAW GROUND BEEF

Concentration(a) Oily Sweet Fragrant 0.2 2.064 2.06 0.88 0.18 5.064 2.06 0.75 0.0 0.05 2.18 1.06 0.35 0.5 2.50 0.67 0.0 0.3 2.50 0.67 0.36 0.2 2.05 0.48 0.24 1.0 1.89 0.42 0.32 0.002 2.67 0.50 0.0 0.5 1.71 0.57 0.19 0.05 1.71 1.29 0.29	Spicy Burnt 0. 53 0. 65 0. 56 0. 94 0. 94 1. 00 0. 61 0. 94 0. 53 0. 94 0. 53 0. 90 0. 26 0. 63 0. 0 0. 94 0. 33 0. 43 0. 64 1. 00	11 Rancid 12 0.47 14 0.83 15 0.63 16 0.63 17 0.63 18 1.06 18 2.19 19 0.38 10 0.38	Anneld Metallic 0.47 0.65 0.88 1.00 0.53 0.88 0.43 0.79 0.90 1.05 0.63 0.47 1.06 0.83 2.19 0.81 0.71 0.57 0.38 0.56	.मू	Sulfurous 0.0 0.44 0.0 0.39 0.0 0.57 0.0 1.00	"D"(c)
0.88 0.75 1.06 0.67 0.48 0.42 0.50 0.57 1.29			0.65 1.00 0.88 1.39 0.79 0.47 0.81 0.81		0. 0 0. 44 0. 0 0. 39 0. 0 0. 57 0. 0	0.83
0.75 1.06 0.67 0.50 0.48 0.42 0.50			0.88 0.79 0.79 0.47 0.83 0.81		0.0 0.0 0.0 0.0 0.0 0.0 0.0	0.00
1.06 0.67 0.50 0.48 0.42 0.50 0.50			0.88 0.79 0.79 0.83 0.83 0.81 0.55		0.39 0.0 0.57 0.0	
0.67 0.50 0.48 0.42 0.50 0.57			1.39 0.79 1.05 0.47 0.83 0.81 0.57		0.0 0.0 0.57 0.0	0.73
0.50 0.48 0.42 0.50 0.57 1.29			0.47 0.47 0.83 0.83 0.57		0.0 0.57 0.0	20.0
0.48 0.42 0.50 0.57 1.29			0.47 0.83 0.81 0.57 0.56		0. 57 0. 0 1. 00	0.93
0.42 0.50 0.57 1.29			0.47 0.83 0.81 0.57		0.0	96.0
0.50 0.57 1.29			0.83 0.81 0.57 0.56		1.00	0.99
0.57			0.81 0.57 0.56		7.00	0.97
0.57 1.29			0.81 0.57 0.56			1. 18
1.29			0.57		9.62	1. 79
			0.56			7
			0.56		•	P 7 . 1
0.81			2		3.3	000
0.44			0.63		3.1	0.72
0.77			0.45			20.00
0.68			1.18		7.27	88
0.74			1,05		. 0	0.93
2.50 1.17 0.0	0.61 0.28		0.89	0.39	7. 22	10.1
1,00			0.50). 42	0.88
1, 14			0.48		7.14	1.11
0.36			0.73		1. 18	2.10
0.24			1.48		٠. 29	1.04
1.00			1.06		7.31	0.94
1.00	0.37 0.68		0.84		، 21	0.54
1, 13			0.63		. 50	1.03
0.65			0.65		1.24	0.72
0.71.			0.95		0.0	0, 63
0.23			0.68		1, 23	1.28
1.21	0.50 0.36		1. 14		. 36	1.41
0.57	0.38 0.53	0	0.95		33	10.1
0.35 0.	0.	0.53			0.47	1.21
2.68 0.64 0.18		0.59	0.77	0.27 0		Values used as reference
						for calculation of D
1.33 0.52 0.19		0.48	0.76	0.14 0	. 19	1. 48
0.64		0.32	0.32 0.91	1, 29 0.82 0.53 0.32 0.91 0.59 0.33 0.38 0.48	1, 29 0.82 0.53 1.00 0.53 0.32 0.91 0.59 0.77 0.27 0.33 0.38 0.48 0.76 0.14	1.29 0.82 0.53 1.00 0.53 0.47 0.32 0.91 0.59 0.77 0.27 0.0 0.33 0.38 0.48 0.76 0.14 0.19

(a) Concentration in µℓ of chemical added per ounce of fresh ground beef.
 (b) Mean values obtained from ratings of 16 to 22 panelists. Word categories were scored from Not similar = 0 to Extremely similar = 8.
 (c) Formula for degree of similarity
 D =√Zd².

(d) For methods of preparation, consult footnotes of Table 11.

TABLE 14. THE EFFECT ON IRRADIATION ODOR INTENSITY OF SELECTED TWO-CHEMICAL BLENDS IN ORDER OF HIGH TO LOW MEAN RATINGS

	Blend	
	(Chemical Concentration Given	Mean Irradiation Odor
Number	in $\mu \ell /oz)$	Intensity Level(a)
(1)	Methyl sulfide 0.05, propanal 0.05	5,83
(2)	Hydrogen sulfide(b) 5.0, methylamine 0.5	5,15
(3)	1-Propanethiol 0.002, methyl sulfide 0.05	4.88
(4)	Methyl sulfide 0.05, 2-butenal 1.0	4.67
(5)	Methyl sulfide 0.05, methylamine 0.5	4.61
(6)	1-Propanethiol 0.02(c), methylamine 0.5	4.44
(7)	1-Propanethiol 0.02(c), pyridine 0.2	4.41
(8)	Carbon disulfide 0.5, acrolein 0.3	4.36
(9)	Hydrogen sulfide 5.0, pyridine 0.2	4.28
(10)	Acetaldehyde 0.3, methylamine 0.5	4. 25
(11)	Methyl sulfide 0.05, pyridine 0.2	4. 19
(12)	Carbon disulfide 0.5, acetaldehyde 0.3	4.17
(13)	Carbon disulfide 0.5, pyridine 0.2	4.00
(14)	1-Propanethiol 0.002, propanal 0.05	3,89
(15)	Propanal 0.05, acrolein 0.3	3, 89
(16)	Methional 0.2, methyl sulfide 0.05	3, 88
(17)	Methional 0.2, acrolein 0.3	3.79
(18)	2-Butenal 1.0, pyridine 0.2	3.78
(19)	Methional 0.2, propanal 0.05	3.77
(20)	1-Propanethiol 0.002, acetaldehyde 3.0(d)	3.56
(21)	Carbon disulfide 0.5, methylamine 0.5	3,44
(22)	Methional 0.2, 2-butenal 1.0	3.44
(2.3)	1-Propanethiol 0.002, methional 0.2	3.43
(24)	Acrolein 0.3, methylamine 0.5(e)	3, 32
(25)	Carbon disulfide 0.5, 2-butenal 1.0	3.08
(26)	Methional 0.2, carbon disulfide 0.5	3.06
(27)	Hydrogen sulfide 10.0, acetaldehyde 3.8	3.00
(28)	Propanal 0.05, pyridine 0.2	2.94
(29)	Methional 0.2, pyridine 0.2	2.71
(30)	1-Propanethiol 0.002, hydrogen sulfide 5.0(e)	2.68
(31)	1-Propanethiol 0.002, acrolein 0.3	2.64
(32)	Hydrogen sulfide 5.0, 2-butenal 1.0	2.56
(33)	Hydrogen sulfide 5.0, acrolein 0.3	2.54
(34)	1-Propanethiol 0.002, 2-butenal 1.0	2.50
	Unirradiated control ground beef	3.63(f)
	Unirradiated control ground beef(e)	2.89
	Unirradiated control ground beef	3, 10
	Unirradiated control ground beef	3,60

⁽a) Each mean value represents 13 to 19 judgements.

⁽b) For preparation procedure, consult Footnote (c) of Table 11.

⁽c) Due to dilution error, the concentration of 1-propanethiol was ten times higher than previously established. A slight onion-like odor was noticeable in the samples.

⁽d) Acetaldehyde was used at ten times the level previously established from single-chemical-addition studies. The odor of acetaldehyde appeared to mask the sulfur-containing compounds.

⁽e) This lot of ground beef was overaged and rancid in odor. It was subsequently discarded.

⁽f) The irradiation odor intensity values for four different lots of control ground beef are presented to indicate the amount of variability observed. During the series of chemical-addition studies, the value dropped approximately one scale point from the value given in Figure 3.

TABLE 13. ODOR DIMENSIONS OF SINGLE CHEMICAL ADDITIONS TO RAW GROUND BEEF

						Mean De	gree of	Mean Degree of Similarity(b)	y(b)			Index of Similarity
Position	Chemical	Concentration(a)	Oily	Sweet	Fragrant	Spicy	Burnt	Rancid	Metallic	Etherish	Sulfurous	"D"(c)
Œ	Pyridine	0.2	2.06	0.88	0.18	0.53	0.65	0.47	0.65	0.59	0.0	0.83
(2)	Hydrogen sulfide	5, 0 ^(d)	2.06	0,75	0.0	0.56	0.94	0.88	1.00	0.50	0, 44	0.93
<u>(c)</u>	Propanal	0.05	2, 18	1.06	0.35	0.94	1,00	0.53	0.88	0.29	0.0	0.93
€	Methylamine	0.5	2,50	0.67	0.0	0.61	0.94	0.83	1.39	0.61	0.39	0.93
(9)	Acrolein	0.3	2.50	0.50	0.36	0.43	0.57	0.43	0.79	0.0	0.0	0.56
9	Methional	0.2	2,05	0.48	0.24	0.53	0.90	0.00	1.05	0.14	0.57	0.99
2	2-Butenal	1.0	1.89	0.42	0.32	0.26	0,63	0.63	0.47	0.0	0.0	0.97
:€	1-Propanethiol	0.002	2,67	0.50	0.0	0.0	0.94	1.06	0.83	0.28	1, 00	1. 18
	(propyl mercaptan)											
6)	Carbon disulfide	0.5	1.71	0.57	0.19	0.33	0.43	2.19	0.81	0.38	0.62	1.79
(10)	Methyl sulfide	0.05	1.71	1.29	0.29	0,64	1,00	0.71	0.57	0.29	0.0	1.24
	(dimethyl sulfide)											
(11)	Acetaldehyde	0.3	1.94	0.81	0.0	0.56	0.88	0.38	0.56	0.31	0.31	0.92
(12)	Methanethiol	0.002	2,00	0.44	0.0	0.44	0.50	0.56	0.63	0.0	0.31	0.95
(13)	2-Propanone	30.0	2,05	0.77	0.14	0.23	0.50	0.55	0.45	0.41	0.0	0.85
(14)	1-Octene	1.0	5.09	99.0	0.32	0.27	0.59	0.41	1. 18	0.41	0.27	0.88
(15)	Octane	-5.0	2, 32	0.74	0.37	0.68	0.63	0.63	1.05	0.0	0.0	0.97
(16)	Ammonia	50.0(d)	2,50	1, 17	0.0	0.61	0.28	0.33	0.89	0.39	0.22	1,01
(17)	Pyrrole	10.0	2,29	1,00	0.0	0.57	0.64	0.57	0.50	0.0	0.42	0.88
(18)	Nonanal	0.1	1,95	1, 14	0.19	0.14	0.43	0,33	0.48	0.14	0.14	1.11
(13)	Methyl disulfide	0.075	1.86	0,36	0.0	0.59	0.68	2.00	0.73	0.64	1, 18	2. 10
(20)	Hexane	100.0	2, 19	0.24	0.29	0.24	98.0	0.57	1.48	0.52	0.29	1.04
(21)	Carbonyl sulfide	50.0(d)	2.81	1,00	0.0	0.56	0.81	0.63	1.06	0.94	0.31	0.94
(22)	2-Butanone	2.0	2.74	1.00	0.37	0.37	0.68	0.53	0.84	0.16	0.21	0.54
(53)	n-Valeraldehyde	0.2	2.81	1. 13	0.0	0.25	1.38	0.81	0.63	0.75	0.50	1.03
(24)	Methanol	500.0	2.41	0,65	0.41	0.41	0.47	0.94	0.65	0.29	0.24	0.72
(52)	Octanol	0.05	2, 43	0.71.	0.0	0.29	0.43	0.43	0.95	0.23	0.0	0.63
(56)	Benzene	5.0 .	1.68	0.23	0.50	0.77	0.77	0.55	0.68	0.0	0.23	1. 28
(23)	Ethanol	500.0	2, 36	1.21	0.86	0.50	0.36	1.14	1.14	0.71	0.36	
(87)	1-Hexene	1.0	1.90	0.57	0.43	0.38	0.53	0.71	0.95	0.48	0.33	1.01
(52)	Toluene	3.0		0.35	0.0	1.29	0.82	0.53	1.00	0.53	0.47	
radiated	Irradiated raw ground beef		2,68	0.64	0.18	0.32	0.91	0.59	0.77	0.27	0.0	Values used as reference
												for calculation of D
nirradia	Thirradiated raw ground heef		1.33	0.52	0.19	0 33	38	0.48	0.76	41.0	0.19	1.48

(a) Concentration in $\mu \ell$ of chemical added per ounce of fresh ground beef.

(b) Mean values obtained from ratings of 16 to 22 panelists. Word categories were scored from Not similar = 0 to Extremely similar = 8.

(c) Formula for degree of similarity $D = \sqrt{\Sigma d^2}.$

(d) For methods of preparation, consult footnotes of Table 11.

TABLE 14. THE EFFECT ON IRRADIATION ODOR INTENSITY OF SELECTED TWO-CHEMICAL BLENDS IN ORDER OF HIGH TO LOW MEAN RATINGS

	Blend	
	(Chemical Concentration Given	Mean Irradiation Odor
Number	in $\mu\ell$ /oz)	Intensity Level(a)
(1)	Methyl sulfide 0.05, propanal 0.05	5,83
(2)	Hydrogen sulfide(b) 5.0, methylamine 0.5	5, 15
(3)	1-Propanethiol 0.002, methyl sulfide 0.05	4.88
(4)	Methyl sulfide 0.05, 2-butenal 1.0	4.67
(5)	Methyl sulfide 0.05, methylamine 0.5	4,61
(6)	1-Propanethiol 0.02(c), methylamine 0.5	4,44
(7)	1-Propanethiol 0.02(c), pyridine 0.2	4.41
(8)	Carbon disulfide 0.5, acroleîn 0.3	4.36
(9)	Hydrogen sulfide 5.0, pyridine 0.2	4.28
(10)	Acetaldehyde 0.3, methylamine 0.5	4, 25
(11)	Methyl sulfide 0.05, pyridine 0.2	4.19
(12)	Carbon disulfide 0.5, acetaldehyde 0.3	4.17
(13)	Carbon disulfide 0.5, pyridine 0.2	4.00
(14)	1-Propanethiol 0.002, propanal 0.05	3.89
(15)	Propanal 0.05, acrolein 0.3	3.89
(16)	Methional 0.2, methyl sulfide 0.05	3.88
(17)	Methional 0.2, acrolein 0.3	3.79
(18)	2-Butenal 1.0, pyridine 0.2	3.78
(19)	Methional 0.2, propanal 0.05	3,77
(20)	1-Propanethiol 0.002, acetaldehyde 3.0(d)	3.56
(21)	Carbon disulfide 0.5, methylamine 0.5	3.44
(22)	Methional 0, 2, 2-butenal 1, 0	3.44
(23)	1-Propanethiol 0.002, methional 0.2	3.43
(24)	Acrolein 0.3, methylamine 0.5(e)	3.32
(25)	Carbon disulfide 0.5, 2-butenal 1.0	3,08
(26)	Methional 0.2, carbon disulfide 0.5	3.06
(27)	Hydrogen sulfide 10.0, acetaldehyde 3.8	3.00
(28)	Propanal 0.05, pyridine 0.2	2.94
(29)	Methional 0.2, pyridine 0.2	2.71
(30)	1-Propanethiol 0.002, hydrogen sulfide 5.0(e)	2.68
(31)	1-Propanethiol 0.002, acrolein 0.3	2.64
(32)	Hydrogen sulfide 5.0, 2-butenal 1.0	2.56
(33)	Hydrogen sulfide 5.0, acrolein 0.3	2.54
(34)	1-Propanethiol 0.002, 2-butenal 1.0	2.50
	Unirradiated control ground beef	3.63(f)
	Unirradiated control ground beef(e)	2.89
	Unirradiated control ground beef	3, 10
	Unirradiated control ground beef	3.60

⁽a) Each mean value represents 13 to 19 judgements.

⁽b) For preparation procedure, consult Footnote (c) of Table 11.

⁽c) Due to dilution error, the concentration of 1-propanethiol was ten times higher than previously established. A slight onion-like odor was noticeable in the samples.

⁽d) Acetaldehyde was used at ten times the level previously established from single-chemical-addition studies. The odor of acetaldehyde appeared to mask the sulfur-containing compounds.

⁽e) This lot of ground beef was overaged and rancid in odor. It was subsequently discarded.

⁽f) The irradiation odor intensity values for four different lots of control ground beef are presented to indicate the amount of variability observed. During the series of chemical-addition studies, the value dropped approximately one scale point from the value given in Figure 3.

TABLE 13. ODOR DIMENSIONS OF SINGLE CHEMICAL ADDITIONS TO RAW GROUND BEEF

						Mean De	gree of	Mean Degree of Similarity(b)	v(b)			Index of Similarity
Position	Chemica1	Concentration(a)	Oily	Sweet	Fragrant	Spicy	Burnt	Rancid	Metallic	Etherish	Sulfurous	'''D'''(c)
Ξ	Pyridine	0.2	2.06	0.88	0.18	0.53	0.65	0.47	0.65	0.59	0.0	0.83
(2)	Hydrogen sulfide	5.0(4)	5.06	0.75	0.0	0.56	0.94	0.88	1,00	0.50	0 44	0 0
(3)	Propanal	0.05	2, 18	1.06	0.35	0.94	1.00	0.53	0.88	0.29	0.0	50 0
€	Methylamine	0.5	2,50	0.67	0.0	0.61	0.94	0.83	1, 39	0.61	0.39	50.00
(2)	Acrolein	0,3	2.50	0.50	0.36	0, 43	0.57	0.43	0.79	0.0) c	0.75
9	Methional	0.2	2.05	0.48	0.24	0.53	0.00	06.0	1.05	0.14	7.5	66
3	2-Butenal	1.0	1.89	0.42	0.32	0.26	6.63	0.63	0.47			0.93
(8)	1-Propanethiol	0.002	2,67	0.50	0.0	0.0	0.94	1.06	0.83	0.28	00.1	2.5
	(propyl mercaptan)									;	}	2
	Carbon disulfide	0.5	1.71	0.57	0.19	0.33	0.43	2, 19	0.81	0,38	0.62	1. 79
(10)	Methyl sulfide	0.05	1.71	1.29	0.29	0.64	1.00	0.71	0.57	0.29	0.0	1.24
	(dimethyl sulfide)											
į	Acetaldehyde	0.3	1.94	0.81	0.0		0.88	0.38	0.56	0.31	0.31	0.92
	Methanethiol	0.002	2.00	0.44	0.0	0.44	0.50	0.56	0.63	0.0	0.31	0.95
	2-Propanone	30.0	2,05	0.77	0.14	0.23	0.50	0.55	0.45	0.41	0.0	0.85
(14)	1-Octene	1.0	2.09	9. 68	0.32	0.27	0.59	0.41	1, 18	0.41	0.27	88.0
(15)	Octane	-5.0	2, 32	0.74	0.37	0.68	0.63	0.63	1.05	0.0	0.0	0.97
·	Ammonia	50.0(d)	2,50	1.17	0.0	0.61	0.28	0.33	0.89	0.39	0.22	1.01
	Pyrrole	10.0	2.29	1,00	0.0	0.57	0.64	0.57	0.50	0.0	0.42	0.88
_	Nonanal	0.1	1,95	1, 14	0.19	0.14	0.43	0,33	0.48	0.14	0.14	1.11
_	Methyl disulfide	0.075	1, 36	0.36	0.0	0.59	99.0	2.00	0.73	0.64	1, 18	2, 10
	Hexane	100.0	2, 19	0.24	0.29	0.24	98.0	0.57	1, 48	0.52	0.29	1.04
_	Carbonyl sulfide	50.0(d)	2.81	1.00	0.0	0.56	0.81	0.63	1.06	0.94	0.31	0.94
	2-Butanone	2.0	2.74	1.00	0.37	0.37	0.68	0.53	0.84	0.16	0.21	0.54
	n-Valeraldehyde	0.2	2.81	1. 13	0.0	0.25	1.38	0.81	0.63	0.75	0.50	1.03
	Methanol	500.0	2.41	0.65	0.41	0.41	0.47	0.94	0.65	0.29	0.24	0.72
	Octanol	0.05	2, 43	0.71.	0.0	0.29	0.43	0.43	0.95	0.23	0.0	0.63
	Benzene	5.0	1.68	0.23	0.50	0.77	0.77	0.55	0.68	0.0	0.23	1.28
_	Ethanol	500.0	2, 36		0.86	0.50	0.36	1.14	1.14	0.71	0.36	17.1
_	l-Hexene	1.0	1.90	0.57	0.43	0.38	0.53	0.71	0.95	0.48	0.33	10.1
(62)	Toluene	3.0	2. 47		0.0	1.29	0.82	0.53	1.00	0.53	0.47	1.21
radiated	Irradiated raw ground beef		2. 68	0.64	0.18	0.32	0.91	0.59	0.77	0.27	0.0	Values used as reference
nirradiat	Unirradiated raw ground beef		1, 33	0.52	0.19	33	38	87	7,4	71	0	. 40

(a) Concentration in $\mu \ell$ of chemical added per ounce of fresh ground beef.

(b) Mean values obtained from ratings of 16 to 22 panelists. Word categories were scored from Not similar = 0 to Extremely similar = 8.

(c) Formula for degree of similarity $D = \sqrt{\Sigma d^2}.$

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	Blend	Manu Tuun dinkinu Oda
Number	(Chemical Concentration Given in $\mu\ell$ /oz)	Mean Irradiation Odo: Intensity Level(a)
(1)	Methyl sulfide 0.05, propanal 0.05	5.83
(2)	Hydrogen sulfide(b) 5.0, methylamine 0.5	5.15
(3)	1-Propanethiol 0.002, methyl sulfide 0.05	4.88
(4)	Methyl sulfide 0.05, 2-butenal 1.0	4,67
(5)	Methyl sulfide 0.05, methylamine 0.5	4.61
(6)	1-Propanethiol 0.02(c), methylamine 0.5	4.44
(7)	1-Propanethiol 0.02(c), pyridine 0.2	4.41
(8)	Carbon disulfide 0.5, acrolein 0.3	4.36
(9)	Hydrogen sulfide 5.0, pyridine 0.2	4.28
(10)	Acetaldehyde 0.3, methylamine 0.5	4, 25
(11)	Methyl sulfide 0.05, pyridine 0.2	4.19
(12)	Carbon disulfide 0.5, acetaldehyde 0.3	4.17
(13)	Carbon disulfide 0.5, pyridine 0.2	4.00
(14)	1-Propanethiol 0.002, propanal 0.05	3,89
(15)	Propanal 0.05, acrolein 0.3	3.89
(16)	Methional 0.2, methyl sulfide 0.05	3, 88
(17)	Methional 0.2, acrolein 0.3	3.79
(18)	2-Butenal 1.0, pyridine 0,2	3.78
(19)	Methional 0.2, propanal 0.05	3.77
(20)	1-Propanethiol 0.002, acetaldehyde 3.0(d)	3.56
(21)	Carbon disulfide 0.5, methylamine 0.5	3.44
(22)	Methional 0.2, 2-butenal 1:0	3.44
(23)	1-Propanethiol 0.002, methional 0.2	3.43
(24)	Acrolein 0.3, methylamine 0.5(e)	3.32
(25)	Carbon disulfide 0.5, 2-butenal 1.0	3,08
(26)	Methional 0.2, carbon disulfide 0.5	3.06
(27)	Hydrogen sulfide 10.0, acetaldehyde 3.8	3.00
(28)	Propanal 0.05, pyridine 0.2	2.94
(29)	Methional 0.2, pyridine 0.2	2.71
(30)	1-Propanethiol 0.002, hydrogen sulfide 5.0(e)	2,68
(31)	1-Propanethiol 0,002, acrolein 0,3	2.64
(32)	Hydrogen sulfide 5.0, 2-butenal 1.0	2.56
(33)	Hydrogen sulfide 5.0, acrolein 0.3	2.54
(34)	1-Propanethiol 0.002, 2-butenal 1.0	2.50
	Unirradiated control ground beef	3,63(f)
	Unirradiated control ground beef(e)	2.89
	Unirradiated control ground beef	3.10
	Unirradiated control ground beef	3.60

⁽a) Each mean value represents 13 to 19 judgements.

⁽b) For preparation procedure, consult Footnote (c) of Table 11.

⁽c) Due to dilution error, the concentration of 1-propanethiol was ten times higher than previously established. A slight onion-like odor was noticeable in the samples.

⁽d) Acetaldehyde was used at ten times the level previously established from single-chemical-addition studies. The odor of acetaldehyde appeared to mask the sulfur-containing compounds.

⁽e) This lot of ground beef was overaged and rancid in odor. It was subsequently discarded.

⁽f) The irradiation odor intensity values for four different lots of control ground beef are presented to indicate the amount of variability observed. During the series of chemical-addition studies, the value dropped approximately one scale point from the value given in Figure 3.

TABLE 15. THE EFFECT ON IRRADIATION ODOR INTENSITY OF MULTIPLE CHEMICAL BLENDS

Number	Blend ^(a)	Irradiation Odor Intensity Mean ^(b)
	No chemical addition, irradiated raw ground beef	6.05
(1)	Methylamine, 2-butenal, methyl sulfide	5.11
(2)	1-Propanethiol, acetaldehyde, methyl sulfide	4.75
(3)	1-Propanethiol, acetaldehyde, methylamine, octane	4,35
(4)	Methyl sulfide, pyridine, acrolein	4.27
(5)	Pyridine, methylamine, acetaldehyde	3.72
(6)	Methylamine, 2-butenal, methyl sulfide, pyridine	3.67
(7)	Propanal, acrolein, 2-butenal	3.58
(8)	1-Propanethiol, propanal, methyl sulfide	3.58
(9)	Methional, methylamine, acetaldehyde, octane	3.19
(10)	Carbon disulfide, acrolein, pyridine	3.05
(11)	Methional, hydrogen sulfide(c), octane	3.00
(12)	1-Propanethiol, methylamine, acetaldehyde, octane	2.82

⁽a) Unless otherwise stated, concentrations of chemicals in the blends were identical to the single-chemical presentations, Table 11.

⁽b) Each mean value is the result of 15 to 19 judgements.

⁽c) Ten μ of a saturated solution of hydrogen sulfide in ethylene glycol per ounce of ground beef. Analyzed at 0.43 per cent hydrogen sulfide.

Method of Sample Preparation

It appeared, during the experimental work, that the methods used to prepare and present samples for panel evaluation were adequate. Throughout the study the irradiation odor intensity data for fresh ground beef supported a hypothesis suggested by Quartermaster personnel that no compound found in irradiated beef is wholly absent from fresh beef. Evidently, according to the methods of evaluation used, people detected odor characteristics in fresh ground beef reminiscent of the odor of the raw irradiated beef standard.

Although use of a fresh ground beef carrier for the chemical appeared the most logical approach in a study of irradiated beef odor, the possibility of formulating a mixture of compounds without the beef carrier to produce "irradiation odor" should not be discounted. Possible carriers of odorants for panel evaluation might be an odorless solvent such as ethylene glycol or a water-soluble fresh beef extract. The latter method might be preferable because it might simulate the fresh ground beef used presently. Studies of this nature might be similar to those mentioned in Phase II of the proposal for the present program.

Sensory Evaluation Methodology

Another primary objective of this program (Phase II of the Proposal) was to develop an appropriate method(s) for evaluating the contribution to irradiated beef odor of single compounds and mixtures of compounds. The two methods selected were submitted to reliability and validity studies as already reported, but it soon became apparent that the only useful evaluation of sensory methodology could be conducted during the actual experimental work. Therefore, the authors considered the evaluation of sensory methodology as one of the accomplishments of the current project. Any constructive discussion will thus include the shortcomings of the methods used and suggestions for future inquiry. Unfortunately, it was not deemed possible to make alterations in sensory methodology during the experimental work on chemicals in fresh ground beef, because rechecking of every sample submitted to panel evaluation would obviously have been necessary and could have been a project in itself.

The rating of irradiation odor intensity was the most useful of the two sensory methods. It appeared to function adequately when used to test dilution of irradiated beef with fresh beef. However, when chemical additions to fresh beef were evaluated, the problem of which chemicals contributed to "irradiation odor" arose. In the first instance, the problem was evidently clearer to the panelists, because the basic odor quality was not altered. In the second instance, the addition of chemical(s) partly masked the "meaty" odor of fresh beef and contributed additional stimuli, probably confusing the panelists. The problem for the panelists thus became one of qualitatively evaluating the relationship to irradiation odor of attributes contributed by chemical addition as well as rating on the intensity scale the quantity of irradiation odor present. It was noted that for a particular sample, disagreement occurred among panelists' ratings regarding what quality of odor constituted an irradiation-like odor, despite the fact the standard irradiated beef sample was always available for reference. Differences of opinion are to be expected in a method of this type; nevertheless, there was a tendency, despite written and oral instructions on the importance of odor quality, to rate a relatively strong odor high on the rating scale.

From the foregoing, it appeared that a method of clarifying the evaluation task would be appropriate. For future work, a matching technique might be employed as mentioned in this and the First Quarterly Report in which the "degree of similarity" scale would be used. Use of such a technique should reduce the problem to a simpler over-all qualitative judgment.

The odor-matching method as applied to the study of irradiated beef odor attributes appeared at the outset of the program to possess great potential. However, certain disadvantages became apparent as the evaluation of single chemicals in fresh beef progressed: (1) all of the population of odor attributes represented by the standard odorants did not apply to the attributes of irradiated beef odor; (2) ratings for any one of the odor attributes seldom exceeded "slight", raising questions as to the meaningfulness of the data; and (3) therefore, chemicals representing odor attributes such as fragrant, spicy, rancid, metallic, etherish, and sulfurous, except in a few observable instances, were not applicable to rating irradiation odor. The attributes used thus might be considered representative of odorants in general but not specific enough to the task. The reliability and validity studies on the odor-matching method demonstrated beyond question its usefulness in evaluating other pure chemical compounds. However, as in the irradiation odor intensity method, the addition of chemical(s) to the ground beef carrier resulted a far more complex evaluation task. Reducing odor intensities of the standard odors by dilution apparently did not alter the odor associations, as previous indicated by the D scores with irradiated beef.

Further effort is needed to develop an odor-matching technique which would be more specific to the evaluation of food odors and, particularly, off-odors as in irradiated beef. It seems clear that nine odorants cannot be used as references for all food odors or off-odors. Possibly, other odorants selected from the 30 studied by QMF&CI would be applicable as meaningful standards, as well as, additional odorants not yet studied. In addition, suitable attribute names might be applied to a mixture of odorants which would correspond more closely to an attribute of irradiated beef. To make the evaluation task less complex, it may be possible to use fewer standard odorants than presently used.

Contribution to Irradiation Odor of Chemicals Isolated From Irradiated Beef

Progress in the sensory identification of those compounds which contribute to irradiation odor should probably be judged by results obtained from the multiple blending experiments which may simulate more closely an irradiated beef sample. However, the value of the one- or two-chemical presentation series was in the possibility that one or two compounds contribute significantly to irradiation odor. The first 11 compounds listed in Table 11, and the first 13 two-chemical blends in Table 14 not only give evidence that their relative contributions to irradiation odor differ, but also that all produce an irradiation odor impression higher than that for fresh ground beef alone.

Unfortunately, due to time limitations, single compounds could not be rechecked for contribution to irradiation odor intensity nor could various concentrations of each be evaluated by panel studies in the fresh ground beef carrier. Thus, the possibility remains that some compounds very important to irradiation odor were not selected for further blending experiments. Evidence of variability in irradiation odor intensity

ratings was obtained by resubmitting methylamine, pyridine, and propanal individually to the panel in the originally established concentrations. Mean ratings were about one scale point lower than previously, but higher than values for the fresh beef carrier rated during the same series of experiments.

From the multiple blending experiments (Table 15) it is clear that methylamine, 2-butenal, methyl sulfide, 1-propanethiol, acetaldehyde, pyridine, and acrolein may be relatively important to irradiation odor. It should be noted that the mean rating for chemical additions to fresh ground beef probably would not exceed the rating for raw irradiated beef presented as an unknown, since the problem of identification and adaptation also exists in this instance.

Future experimentation should consist of a thorough screening of all possible combinations of compounds found in the current study to contribute to irradiation odor of beef. In addition, the number of compounds per blend should be increased to simulate the actual complex situation in irradiated beef. A modification of the sample-preparation procedure will likely be necessary so that the physical identity of the ground beef carrier would not be significantly altered. This may possibly be accomplished by diluting some or all of the odorants together in a mixture and adding to the fresh ground beef. Within the blends, concentrations of individual odorants may have to be changed to prevent one odorant from masking odors contributed by others. Other compounds from this and other studies should be included for evaluation or re-evaluation. Obviously, the studies suggested above could result in a large number of possible odorant blends. Because of this, much of the screening work would of necessity have to be accomplished in the laboratory, to reduce the number of chemical combinations and costs involved with sensory panel studies.

PERCENTAGE OF WORK AND COST DATA

Expenditures for the contract period, 14 January 1961 through 13 January 1963, were \$43,495 which represents 100 per cent of the total funds allocated and work completed.

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